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(71) Applicant *(for all designated States except US)*: **AVENTIS CROPSCIENCE GMBH** [DE/DE]; Brüningstrasse 50, D-65929 Frankfurt am Main (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **COOKE, Tracey** [GB/GB]; 7 Larch Avenue, Brickett Wood, St Albans AL2 3SN (GB). **HARDY, David** [GB/GB]; 46 St. Bedes Gardens, Cambridge CB1 3UF (GB). **MOLONEY, Brian, Anthony** [GB/GB]; 2 Crookdale Beck, Oxon OX11 7US (GB). **O'MAHONY, Mary, Josephine** [GB/GB]; 8 Manger's Lane, Duxford, Cambridge CB2 4RN (GB). **PETTETT, Michael, George** [GB/GB]; Aventis CropScience UK Ltd., Fyfield Road, Ongar Essx CM5 OHW (GB). **PATEL, Gita** [GB/GB]; Chesterfield House, Wulfstan Way, Cambridge CB1 8QL (GB). **SCHNATTERER, Stefan** [DE/DE]; Schillerring 10, D-65795 Hattersheim (DE).

(74) Agent: **MERIGEAULT, Shona**; Aventis CropScience S.A., B.P. 9163, F-69263 Lyon Cedex 09 (FR).

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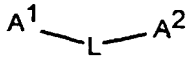
(54) Title: FUNGICIDES



(I)

(57) Abstract: Use of compounds of general formula (I) or salts thereof as phytopathogenic fungicides wherein the various radicals and substituents are as defined in the description, pesticidal compositions containing them and method for combatting pests which comprises applying these.

R^3 and R^4, which may be the same or different, are R^b, cyano or nitro (R^3 and R^4 are preferably hydrogen, acyl or optionally substituted alkyl);

or any R^1, R^2, R^3 or R^4 group, together with the interconnecting atoms, can form a 5- or 6-membered ring with any other R^1, R^2, R^3 or R^4, or any R^1, R^2, R^3 or R^4 group, together with the interconnecting atoms can form a 5- or 6-membered ring with A^2;

X is oxygen, sulfur, N-OR^b, N-R^b or N-$N(R^b)_2$ (X is preferably oxygen or sulfur); and

Y is halogen, $-OR^b$, $-SR^b$, $-N(R^b)_2$, $-NR^b(OR^b)$ or $-NR^bN(R^b)_2$;

wherein R^b is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or hydrogen or acyl, or two adjacent R^b groups together with the nitrogen atom to which they are attached may form a 5- or 6-membered ring.

Preferred substituents on the 2-pyridyl group (A^1) are halogen, hydroxy, cyano, nitro, SF_5, trialkylsilyl, optionally substituted amino, acyl, or a group $-R^a$, $-OR^a$ or $-SR^a$, or a group $-C(R^a)=N-Q$, where Q is $-R^a$, $-OR^a$, $-SR^a$ or optionally substituted amino, wherein R^a is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or two adjacent substituents together with the atoms to which they are attached form an optionally substituted ring which can contain up to 3 hetero atoms. Especially preferred substituents are alkoxy, alkyl, cyano, halogen, nitro, alkoxycarbonyl, alkylsulfinyl, alkylsulfonyl and trifluoromethyl, particularly chlorine and trifluoromethyl.

Preferably, the 2-pyridyl group is substituted at the 3 and/or 5 position.

The invention also includes any of the compounds specifically exemplified hereinafter.

Any alkyl group may be straight or branched and is preferably of 1 to 10 carbon atoms, especially 1 to 7 and particularly 1 to 5 carbon atoms.

Any alkenyl or alkynyl group may be straight or branched and is preferably of 2 to 7 carbon atoms and may contain up to 3 double or triple bonds which may be conjugated, for example vinyl, allyl, butadienyl or propargyl.

group are alkyl, haloalkyl, alkoxy, haloalkoxy or alkylthio, each containing 1 to 5 carbon atoms; halogen; or optionally substituted phenyl.

In the case of any alkyl group or any unsaturated ring-carbon in any carbocyclyl or heterocyclyl group the list includes a divalent group such as oxo or imino, which may be substituted by optionally substituted amino, R^a or $-OR^a$. Preferred groups are oxo, imino, alkylimino, oximino, alkyloximino or hydrazono.

Any amino group, when substituted and where appropriate, may be substituted by one or two substituents which may be the same or different, selected from the list: optionally substituted alkyl, optionally substituted amino, $-OR^a$ and acyl groups. Alternatively two substituents together with the nitrogen to which they are attached may form a heterocyclyl group, preferably a 5 to 7-membered heterocyclyl group, which may be substituted and may contain other hetero atoms, for example morpholino, thiomorpholino or piperidinyl.

The term acyl includes the residues of sulfur and phosphorus-containing acids as well as carboxylic acids. Typically the residues are covered by the general formulae $-C(=X^a)R^c$, $-S(O)_pR^c$ and $-P(=X^a)(OR^a)(OR^a)$, where appropriate X^a is O or S, R^c is as defined for R^a, $-OR^a$, $-SR^a$, optionally substituted amino or acyl; and p is 1 or 2. Preferred groups are $-C(=O)R^d$, $-C(=S)R^d$, and $-S(O)_pR^d$ where R^d is alkyl, C_1 to C_5 alkoxy, C_1 to C_5 alkylthio, phenyl, heterocyclyl or amino, each of which may be substituted.

Complexes of compounds of the invention are usually formed from a salt of formula MAn_2, in which M is a divalent metal cation, e.g. copper, manganese, cobalt, nickel, iron or zinc and An is an anion, e.g. chloride, nitrate or sulfate.

In cases where the compounds of the invention exist as the E and Z isomers, the invention includes individual isomers as well as mixtures thereof.

In cases where compounds of the invention exist as tautomeric isomers, the invention includes individual tautomers as well as mixtures thereof.

alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and *N*-methyl taurine; the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate; acid derivatives of alkyl glycosides and alkylpolyglycosides materials and their metal salts, e.g. alkyl polyglycoside citrate or tartrate materials; or mono-, di- and tri-alkyl esters of citric acid and their metal salts.

Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene and/or propylene oxide; fatty esters of polyhydric alcohol ethers. e.g. sorbitan fatty acid esters; condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters; alkyl glycosides, alkyl polyglycoside materials; block copolymers of ethylene oxide and propylene oxide; acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, ethoxylated acetylenic glycols; acrylic based graft copolymers; alkoxylated siloxane surfactants; or imidazoline type surfactants, e.g. 1-hydroxyethyl-2-alkylimidazoline.

Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide, polyoxyethylene alkylamine or polyoxypropylene alkylamine; an amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, an aerosol, a dispersion, an aqueous emulsion, a microemulsion, a dispersible concentrate, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate, granules or an impregnated strip. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

be intimately mixed with the soil such as by spraying, by broadcasting a solid form of granules, or by applying the active ingredient at the same time as drilling by inserting it in the same drill as the seeds. A suitable application rate is within the range of from 5 to 1000 g per hectare, more preferably from 10 to 500 g per hectare.

Alternatively the active compound can be applied directly to the plant by, for example, spraying or dusting either at the time when the fungus has begun to appear on the plant or before the appearance of fungus as a protective measure. In both such cases the preferred mode of application is by foliar spraying. It is generally important to obtain good control of fungi in the early stages of plant growth, as this is the time when the plant can be most severely damaged. The spray or dust can conveniently contain a pre- or post-emergence herbicide if this is thought necessary. Sometimes, it is practicable to treat the roots, bulbs, tubers or other vegetative propagule of a plant before or during planting, for example, by dipping the roots in a suitable liquid or solid composition. When the active compound is applied directly to the plant a suitable rate of application is from 0.025 to 5 kg per hectare, preferably from 0.05 to 1 kg per hectare.

In addition, the compounds of the invention can be applied to harvested fruits, vegetables or seeds to prevent infection during storage.

In addition, the compounds of the invention can be applied to plants or parts thereof which have been genetically modified to exhibit a trait such as fungal and/or herbicidal resistance.

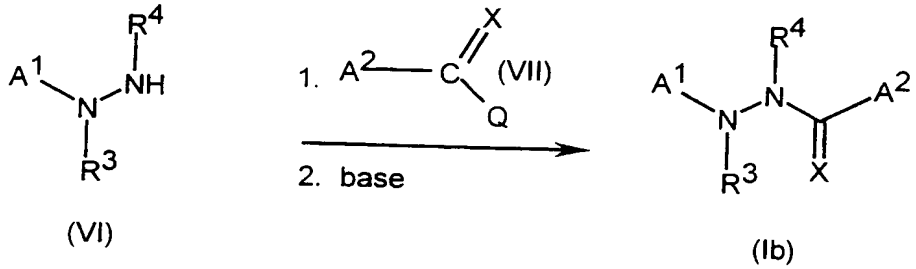
In addition the compounds of the invention can be used to treat fungal infestations in timber and in public health applications. Also the compounds of the invention can be used to treat insect and fungus infestations in domestic and farm animals.

Compounds of the invention may be prepared, in known manner, in a variety of ways.

Compounds of formula Iai, i.e. compounds of general formula I where L is $-CH(R^1)NHCH(R^2)-$, may be prepared according to reaction scheme 1. Compounds of formula II or their hydrochloride salts can be condensed with compounds of formula III and the intermediate reduced with a suitable reagent such as sodium cyanoborohydride to give compounds of formula Iai.

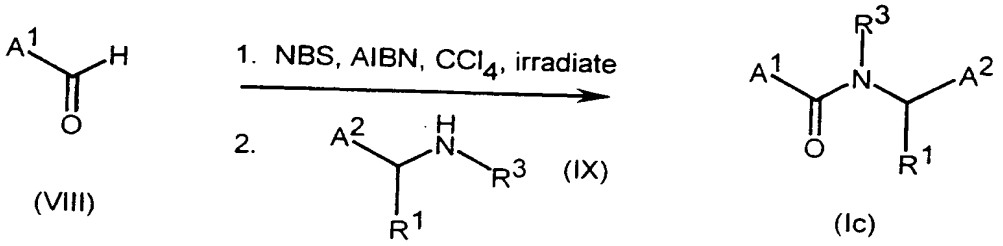
compounds of formula VI with compounds of formula VII, where Q is a leaving group such as halogen, preferably chlorine. A preferred base is triethylamine.

Scheme 4



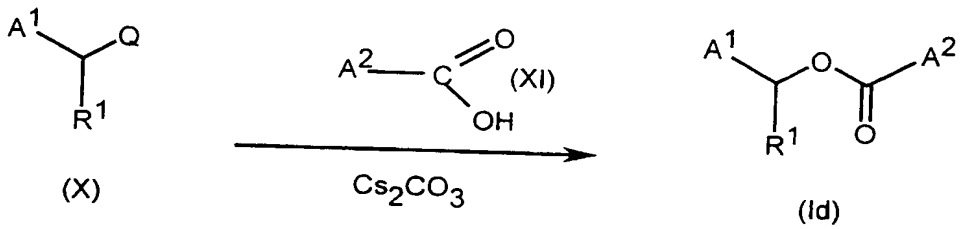
Compounds of formula Ic, i.e. compounds of general formula I where L is $-C(=O)N(R^3)CH(R^1)-$, may be prepared by radical bromination of compounds of formula VIII, followed by reaction of these intermediates with compounds of formula IX according to scheme 5. Preferred reaction conditions are irradiation of a solution of VIII in carbon tetrachloride in the presence of *N*-bromosuccinimide and a catalytic amount of 2,2'-azobisisobutyronitrile, followed by addition of IX..

Scheme 5

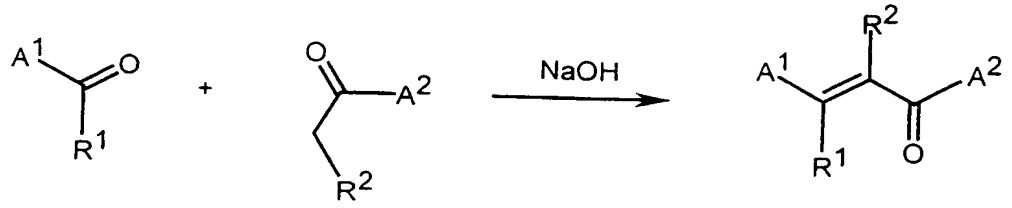


Compounds of formula Id, i.e. compounds of general formula I where L is $-CH(R^1)O(C=O)-$, may be prepared according to reaction scheme 6 by formation of the cesium salt of compounds of formula XI, followed by reaction with compounds of formula X where Q is a suitable leaving group, such as chlorine.

Scheme 6



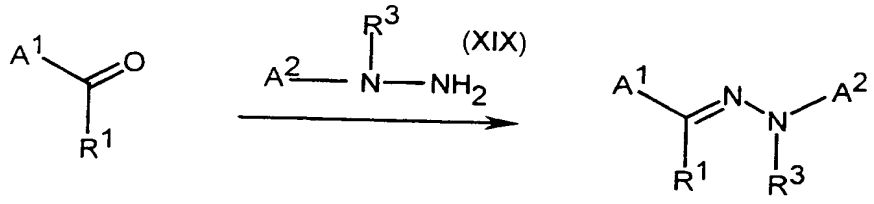
Scheme 9



(XVI) (XVII) (Ig)

Compounds of formula Ih, i.e. compounds of general formula I where L is $-C(R^1)=N-N(R^3)-$, may be prepared by reacting compounds of formula XVIII with compounds of formula XIX according to reaction scheme 10.

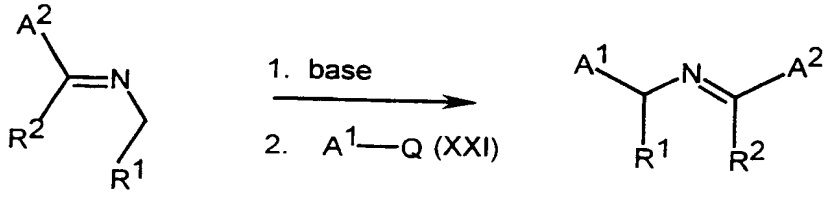
Scheme 10



(XVIII) (Ih)

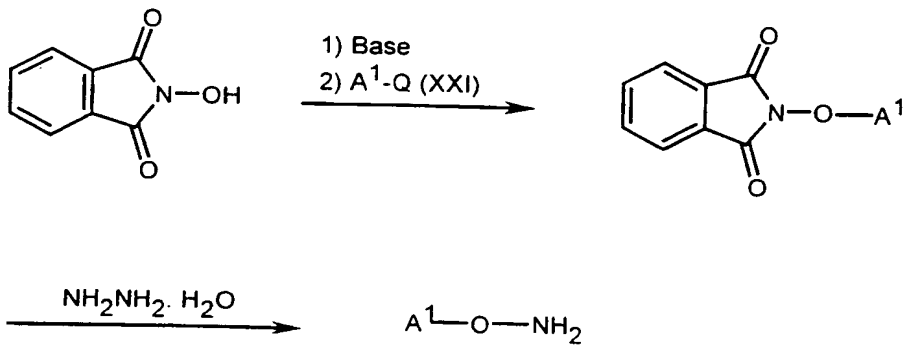
Compounds of formula Ii, i.e. compounds of general formula I where L is $-CH(R^1)N=C(R^2)-$, may be prepared according to reaction scheme 11 by reacting compounds of formula XX with a base, followed by reaction with compounds of formula XXI, where Q is a suitable leaving group, preferably chlorine. A suitable base is sodium hydride. Compounds of formula XX are known or can be prepared in a known manner by a skilled chemist.

Scheme 11



(XX) (Ii)

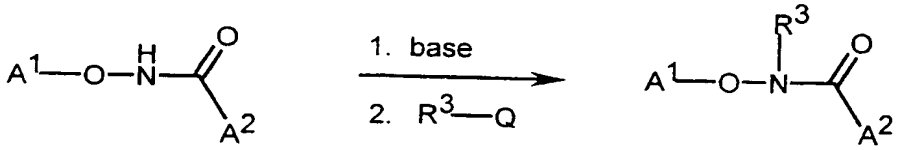
Scheme 15



(XXIII)

Compounds of formula Imii, i.e. compounds of general formula I where L is -O-N(R^3)C(=O)- wherein R^3 is not hydrogen, may be prepared by reaction of compounds of formula Imi with a base, followed by reaction with R^3Q, where Q is a suitable leaving group, such as a halogen. A suitable base is potassium *tert*-butoxide (Scheme 16).

Scheme 16



(Imi) (Imii)

Other methods will be apparent to the chemist skilled in the art, as will be the methods for preparing starting materials and intermediates.

Collections of compounds of formula I may also be prepared in a parallel manner, either manually, automatically or semi-automatically. This parallel preparation may be applied to the reaction procedure, work-up or purification of products or intermediates. For a review of such procedures see by S.H. DeWitt in "Annual Reports in Combinatorial Chemistry and Molecular Diversity: Automated synthesis", Volume 1, Verlag Escom 1997, pages 69 to 77.

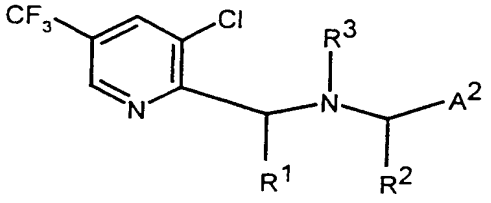
Furthermore, compounds of the formula I may be prepared using solid-supported methods, where the reactants are bound to a synthetic resin. See for example: Barry A. Bunin in "The

Example 3

Ethyl 2-[acetyl(benzyl)amino]-2-[3-chloro-5-(trifluoromethyl)-2-pyridyl]acetate (Compound 4)

To a solution of compound 1 (0.6 mmol) in diethyl ether was added triethylamine (0.7 mmol) followed by acetyl chloride in diethyl ether (0.7 mmol). The mixture was stirred for two hours at room temperature before the addition of hydrochloric acid (8 ml, 2M). The organic phase was isolated, washed with sodium bicarbonate (10ml), dried over magnesium sulfate and evaporated to yield the title compound, ^{1}H N.M.R ($CDCl_3$) (ppm) δ1.2 (3H, t), 2.3 (3H, s), 4.2 (2H, q), 4.8 (2H, q), 6.8-7.1 (6H, m), 7.5 (1H, s) and 8.5 (1H, s).

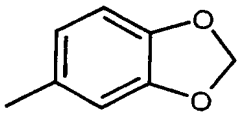
The following compounds of formula Iz (see Table A), i.e. compounds of general formula I where A^1 is 3-Cl-5-CF_3-2-pyridyl and L is $-CH(R^1)N(R^3)CH(R^2)-$, may be prepared by methods analogous to those of Examples 1, 2 and 3. The amine starting materials were obtained using methods described in international application PCT/GB/99/00304.



(Iz)

Table A

Cmp	R^1	R^2	R^3	A^2	m.p./°C
1	EtOC(=O)-	H	H	phenyl	oil
2	EtOC(=O)-	H	H	2-Cl-phenyl	oil
3	EtOC(=O)-	H	H	3,4-methylenedioxyphenyl	oil
4	EtOC(=O)-	H	MeC(=O)-	phenyl	oil
5	EtOC(=O)-	H	$MeOCH_2C(=O)$-	phenyl	oil
6	EtOC(=O)-	H	MeOC(=O)-C(=O)-	phenyl	104-7
7	EtOC(=O)-	H	MeC(=O)-	2-Cl-phenyl	77-81
8	EtOC(=O)-	H	$MeOCH_2C(=O)$-	2-Cl-phenyl	oil
9	EtOC(=O)-	H	MeOC(=O)-C(=O)-	2-Cl-phenyl	128-31
10	EtOC(=O)-	H	MeC(=O)-	3,4-methylenedioxyphenyl	oil

Cmp	R^1	R^2	R^3	A^2	m.p./°C
39	Me	H	H	2-Cl-6-F-phenyl	oil
40	Me	H	H	2-Br-phenyl	oil
41	Me	H	H	3-CF_3O-phenyl	oil
42	Me	H	H	4-MeS-phenyl	oil
43	Me	H	H	2,5-xylyl	oil
44	H	H	H	cyclohexyl	oil
45	H	H	H	3-Br-phenyl	oil
46	H	H	H	4-Me_2N-phenyl	oil
47	H	H	H	4-Cl-phenyl	oil
48	H	H	H	2-F-phenyl	oil
49	H	H	H	2,5-diMeO-phenyl	oil
50	H	H	H	2-Br-phenyl	oil
51	H	H	H	4-NO_2-phenyl	oil
52	H	H	H	2,5-xylyl	oil
53	H	Me	H		oil
54	H	H	H	pentaF-phenyl	oil

The ^{1}H N.M.R. or mass spectral data of those compounds in Table A which were not solid at room temperature are presented below.

Compound 1

^{1}H N.M.R ($CDCl_3$) δ (ppm) 1.2 (3H, t), 2.9 (1H, broad s), 3.8 (1H, q), 4.2 (2H, m), 5.0 (1H, s), 7.4-7.2 (5H, m), 7.9 (1H, s), 8.7 (1H, s).

Compound 2

^{1}H N.M.R ($CDCl_3$) δ (ppm) 1.2 (3H, t), 3.1 (1H, broad s), 4.0 (2H, q), 4.2 (2H, m), 5.1 (1H, s), 7.5-7.2 (4H, m), 8.0 (1H, s), 8.7 (1H, s).

Compound 16

^{1}H N.M.R ($CDCl_3$) δ(ppm) 2.7 (1H, broad s), 4.05 (4H, s), 6.9-7.2 (3H, m), 7.8 (1H, s), 8.6 (1H, s).

Compound 17

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.4 (3H, d), 2.5 (1H, broad s), 3.9 (2H, m), 4.3 (1H, q), 7.1-7.3 (3H, m) 7.5 (1H, m) 7.8 (1H, s), 8.7 (1H, s).

Compound 18

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.5 (3H, d), 2.6 (1H, broad s), 3.8 (1H, m), 4.0 (1H, m) 4.3 (1H, q), 6.8 (2H, m) 7.1 (1H, m) 7.8 (1H, s) 8.6 (1H, s).

Compound 19

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.4 (3H, d) 2.6 (1H, broad s), 3.8 (1H, q), 4.0 (2H, s), 4.3 (4H, s) 6.8 (2H, s), 6.9 (1H, s), 7.9 (1H, s), 8.7 (1H, s).

Compound 20

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.5 (3H, d), 2.4 (3H, s), 2.8 (1H, broad s), 3.8 (1H, q), 4.0 (2H, m), 7.2 (2H, d), 7.3 (2H, d), 7.8 (1H, s), 8.7 (1H, s).

Compound 21

^{1}H N.M.R ($CDCl_3$) δ(ppm) 2.5 (1H, broad s), 4.0 (2H, s), 4.1 (2H, s), 6.8 (2H, m), 7.2 (1H, m), 7.8 (1H, s), 8.6 (1H, s).

Compound 22

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.4 (3H, d), 2.5 (1H, broad s), 3.86 (2H, s), 3.9 (1H, m), 7.5 (2H, d), 7.8 (1H, s), 8.1 (2H, d), 8.7 (1H, s).

Compound 23

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.4 (3H, d), 2.6 (1H, broad s), 3.8 (1H, q), 3.9 (1H, s), 7.1–7.3 (3H, m), 7.9 (1H, s), 8.8 (1H, s).

Compound 33

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.42 (3H, d), 2.62 (1H, broad, s), 3.83 (1H, q), 3.92 (2H, s), 7.3 (4H, s), 7.82 (1H, s); 8.75 (1H, s).

Compound 34

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.42 (3H, d), 2.58 (1H, s, broad), 3.82 (1H, q), 3.92 (2H, s), 7.25 (2H, m), 7.45 (2H, m), 7.85 (1H, s), 8.72 (1H, s).

Compound 35

^{1}H N.M.R ($CDCl_3$) δ(ppm) selected peaks at 1.38 (3H, d), 4.35 (1H, q), 7.85 (1H, s), 8.75 (1H, s).

Compound 36

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.38 (3H, d), 2.35 (1H, broad, s), 3.68 (2H, m), 4.42 (1H, q), 6.95 (1H, m), 7.05 (1H, m), 7.16 (1H, m), 7.32 (1H, m), 7.82 (1H, s), 8.75 (1H, s).

Compound 37

^{1}H N.M.R ($CDCl_3$) δ(ppm) selected peaks at 1.38 (3H, d), 3.56 (2H, m), 4.4 (1H, q), 7.88 (1H, s), 8.78 (1H, s).

Compound 39

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.3 (3H, d), 2.7 (1H, broad, s), 3.8 (2H, s), 4.4 (1H. q), 6.75 (1H, m), 6.98 (2H, m), 7.72 (1H, s), 8.55 (1H, s).

Compound 40

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.41 (3H, d), 2.3 (1H, broad, s), 3.72 (2H, m), 4.25 (1H, q), 7.05-7.5 (4H, m), 7.85 (1H, s), 8.75 (1H, s).

Compound 41

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.38 (3H, d), 2.4 (1H, s, broad), 3.6 (2H, m), 4.4 (1H, q), 7.05-7.5 (4H, m), 7.88 (1H, s), 8.78 (1H, s).

Compound 50

^{1}H N.M.R ($CDCl_3$) δ(ppm) selected peaks at 4.0 (2H, s), 4.1 (2H, s), 7.85 (1H, s), 8.70 (1H, s).

Compound 51

^{1}H N.M.R ($CDCl_3$) δ(ppm) selected peaks at 2.65 (1H, broad, s), 3.83 (2H, s), 4.0 (2H, s), 7.8 (1H, s), 8.65 (1H, s).

Compound 52

^{1}H N.M.R ($CDCl_3$) δ(ppm) selected peaks at 3.83 (2H, s), 4.18 (2H, s), 7.9 (1H, s), 8.75 (1H, s).

Compound 53

^{1}H N.M.R ($CDCl_3$) δ(ppm) 1.4 (3H, d), 2.5 (1H, broad s), 3.8 (1H, q), 3.9 (2H, s), 6.0 (2H, s), 6.8-6.9 (3H, m), 7.9 (1H, s), 8.7 (1H, s).

Compound 54

^{1}H N.M.R ($CDCl_3$) δ(ppm) selected peaks at 7.75 (1H, s), 8.80 (1H, s).

Example 4

N'-1-[3-Chloro-5-(trifluoromethyl)-2-pyridyl]-2,6-dichloro-1-benzenecarbohydrazide (Compound 102)

3-Chloro-5-(trifluoromethyl)pyrid-2-ylhydrazine (0.32 g) was dissolved in dichloromethane (7 ml) and treated dropwise with 2,6-dichlorobenzoyl chloride (0.31 g) in dichloromethane (2 ml). Triethylamine (0.15 g) was then added and the reaction stirred at room temperature overnight. The organic solution was washed sequentially with sodium bicarbonate solution and brine and evaporated to give a solid. The residue was purified by trituration (dichloromethane) to give the title compound, m.p. 212-5 °C.

The following compounds of formula Iy (see Table B), i.e. compounds of general formula I where L is $-N(R^3)NHC(=O)-$, may be prepared by methods analogous to those of Example 4.

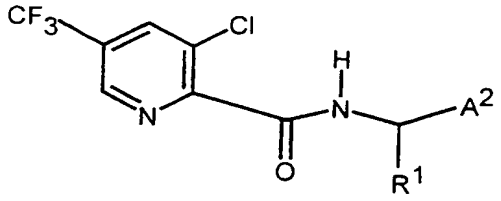
Cmp	A^1	R^3	A^2	m.p./°C
125	3-Cl-5-CF_3-phenyl	H	2,3,6-triF-phenyl	154-6
126	3-Cl-5-CF_3-phenyl	H	2-Cl-6-F-phenyl	192

Example 5

N-2-(Phenylethyl)-3-chloro-5-(trifluoromethyl)-2-pyridinecarboxamide (Compound 206)

3-Chloro-(5-trifluoromethyl)pyridine-2-carboxaldehyde (0.15 g) was dissolved in carbon tetrachloride (10 ml). 2,2'-Azobisisobutyronitrile (0.002 g) and *N*-bromosuccinimide (0.16 g) were added and the mixture was heated to reflux using a sun lamp. After 45 minutes the solution was cooled down to 0 °C. (R)-(+)-α-methylbenzylamine (0.09 g) in carbon tetrachloride (0.3 ml) was added and stirred for 20 minutes at 0°C, then for 3 hours at room temperature. The mixture was diluted with dichloromethane and washed with water. The organic layer was isolated, dried over magnesium sulphate and evaporated to give the crude compound. The crude material was purified by silica gel chromatography to give the title product, m.p. 88 °C.

The following compounds of formula Ix (see Table C), i.e. compounds of general formula I where A^1 is 3-Cl-5-CF_3-2-pyridyl and L is –C(=O)NHCH(R^1)-, may be prepared by methods analogous to those of Example 5.

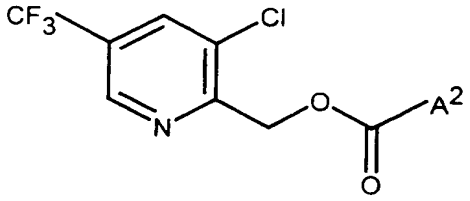


(Ix)

Table C

Cmp	R^1	A^2	m.p.(°C)
201	H	2,6-diF-phenyl	137
202	Me	2,6-diF-phenyl	97
203	H	2-Cl-phenyl	100-7
204	H	2,6-diCl-phenyl	114-6

The following compounds of formula Iw (see Table D), i.e. compounds of general formula I where A^1 is 3-Cl-5-CF_3-2-pyridyl and L is $-CH_2O(C=O)-$, may be prepared by methods analogous to those of Example 6.



(Iw)

Table D

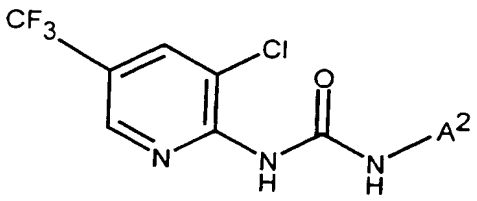
Cmp	A^2	m.p./°C
301	2-Cl-phenyl	oil
302	2,6-diCl-phenyl	93-5

Example 7

[3-Chloro-5-(trifluoromethyl)-2-pyridyl]methyl(2,4-dichlorobenzyl) ether (Compound 401)

To a solution of 2,4-dichlorobenzyl alcohol (0.27 g) in tetrahydrofuran under nitrogen was added sodium hydride (1.1 equivalents) portionwise. The resulting solution was stirred at room temperature for 1 hour before the addition of 3-chloro-2-(chloromethyl)-5-trifluoromethyl pyridine (0.35 g) in tetrahydrofuran dropwise. The solution was then stirred at room temperature for 16 hours. The solution was treated with a tetrahydrofuran/methanol solution and the solvent then evaporated. The residue was partitioned between water and ethyl acetate, the organic phase was isolated, washed with brine, dried and evaporated to yield the crude product. Silica gel chromatography (petrol/ethyl acetate 95:5) furnished the title compound, ^1H N.M.R ($CDCl_3$) δ(ppm) 4.8 (2H, s), 4.9 (2H, s), 7.3 (1H, m), 7.4 (1H, m), 7.5 (1H, m) 8.0 (1H, s) and 8.8 (1H, m).

The following compounds of formula Iv (see Table E), i.e. compounds of general formula I where A^1 is 3-Cl-5-CF_3-2-pyridyl and L is $-CH_2OCH_2-$, may be prepared by methods analogous to those of Example 7.



(Iu)

Table F

Cmp	A^2	m.p./°C
501	2,6-diCl-phenyl	155-8
502	phenyl	173-5
503	2-NO_2-phenyl	178-80

Example 9

3-[3-Chloro-5-(trifluoromethyl)-2-pyridyl]-1-(2-nitrophenyl)-2-propen-1-one (Compound 601)

Sodium hydroxide (0.55 g) was dissolved in water (5 ml) and the resulting solution was diluted with ethanol (3 ml). 2-Nitroacetophenone (1.8 g) was added at 20°C, and the solution was stirred for 5 minutes. 3-Chloro-5-(trifluoromethyl)pyridine-2-carboxaldehyde (2.25 g) was added and stirring was continued for 16 hours. The solution was acidified with acetic acid, the organic layer separated, dried over magnesium sulfate, filtered and evaporated to give a brown oil. Silica gel column chromatography, followed by recrystallisation (petrol) afforded the title compound, 88-9 °C.

Example 10

3-Chloro-5-(trifluoromethyl)-2-pyridinecarbaldehyde 2-(2-nitrophenyl)hydrazone (Compound 701)

A mixture of 3-chloro-5-(trifluoromethyl)pyridine-2-carboxaldehyde (1.05 g) and 2-nitrophenylhydrazine (0.76 g) in ethanol (75 ml) was heated at reflux for 2.5 hours and then allowed to cool to room temperarure overnight. The resulting orange solid was isolated by filtration and recrystallised (petrol) to afford the title compound as a mixture of isomers, m.p. 127-35 °C.

The mass spectral data of the compound in Table G which was not solid at room temperature is presented below.

Compound 802

m/z (EI) 373 (M^+-CO_2Et)

Example 12

1-Biphenylyl-1-ethanone *O*-1-[3-chloro-5-(trifluoromethyl)-2-pyridyl] oxime (Compound 936)

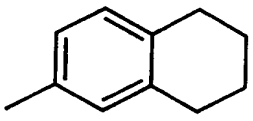
To 4-acetylbiphenyl oxime (2.5 g) in dimethylformamide (13 ml) under a nitrogen atmosphere was added sodium hydride (0.5 g) portionwise with cooling. The resulting mixture was stirred at 40°C for 20 minutes until the formation of a suspension occurred. 2,3-Dichloro-5-(trifluoromethyl)pyridine (2.5 g) in dimethylformamide (7 ml) was then added and the resulting mixture stirred for 18 hours at room temperature. The mixture was treated with isopropanol (2 ml) and stirred for 5 minutes before pouring into an ice water/brine solution (300 ml). The resulting precipitate was extracted with diethyl ether (2x125 ml), the organics washed with water, dried, filtered and evaporated to give a solid which on trituration (diethyl ether) and recrystallisation (toluene) yielded the title compound, m.p. 122 °C.

Preparation of Starting Material

4-Acetylbiphenyl Oxime

To a suspension of 4-acetylbiphenyl (25.4 g) in ethanol (230 ml) and water (4 ml) under a nitrogen atmosphere was added hydroxylamine hydrochloride (14.5 g) in water (25 ml) followed by 50% aqueous potassium hydroxide solution (40 g). The resulting mixture was heated at reflux for 18 hours and then cooled to room temperature. The mixture was added to ice/water (500 ml) and acidified to pH 2 to give a precipitate. The solid was filtered off, washed with water until the washings were at pH 6 and then recrystallised from ethanol to give the title compound.

The following compounds of formula Is (see Table H), i.e. compounds of general formula I where L is –O-N=C(R^1)-, may be prepared by methods analogous to those of Example 12.

Cmp	A^1	R^1	A^2	m.p.(°C)
922	3-Cl-5-CF_3-2-pyridyl	Et	phenyl	oil
923	3-Cl-5-CF_3-2-pyridyl	H	3-NO_2-phenyl	116-8
924	3-Cl-5-CF_3-2-pyridyl	CF_3	2-tolyl	oil
925	3-Cl-5-CF_3-2-pyridyl	$(EtO)_2P(=O)$-	cyclohexyl	oil
926	3-Cl-5-CF_3-2-pyridyl	-CN	phenyl	76
927	3-Cl-5-CF_3-2-pyridyl	Me	phenyl	oil
928	3-Cl-5-CF_3-2-pyridyl	H	2-NO_2-phenyl	oil
929	3-Cl-5-CF_3-2-pyridyl	H	2-Cl-phenyl	87
930	3-Cl-5-CF_3-2-pyridyl	H	3-tolyl	oil
931	3-Cl-5-CF_3-2-pyridyl	H	3-pyridyl	oil
932	3-Cl-5-CF_3-2-pyridyl	H	3-pyridyl	137-8
933	3-Cl-5-CF_3-2-pyridyl	H	1-naphthyl	85-90
934	3,5-diCl-2-pyridyl	Me	2-Cl-phenyl	127
935	3,5-diCl-2-pyridyl	Me	2-Cl-phenyl	70-1
936	3-Cl-5-CF_3-2-pyridyl	Me	biphenylyl	122
937	3-Cl-5-CF_3-2-pyridyl	-CN	2,6-diCl-phenyl	128-9
938	3-Cl-5-CF_3-2-pyridyl	-CN	2,6-diCl-phenyl	71-2
939	3-Cl-5-CF_3-2-pyridyl	-CN	2-CN-phenyl	139-43
940	3-Cl-5-CF_3-2-pyridyl	-CN	2-Cl-phenyl	83-4
941	3-Cl-5-CF_3-2-pyridyl	-CN	2-Cl-phenyl	88
942	3-Cl-5-CF_3-2-pyridyl	Me	2-$MeSO_2$-phenyl	oil
943	3-Cl-5-CF_3-2-pyridyl	Ph	2-naphthyl	oil
944	3-Cl-5-CF_3-2-pyridyl	Me	6-MeO-2-naphthyl	oil
945	3-Cl-5-CF_3-2-pyridyl	Me	4-F-1-naphthyl	oil
946	3-Cl-5-CF_3-2-pyridyl	Me	4-cyclohexyl-phenyl	oil
947	3-Cl-5-CF_3-2-pyridyl	Me		oil
948	3-Cl-5-CF_3-2-pyridyl	Pr	4-Cl-phenyl	oil
949	3-Cl-5-CF_3-2-pyridyl	Me	cyclohexyl	oil

Compound 912

m/z (EI) 357 (M^+).

Compound 913

m/z (EI) 320 (M^+).

Compound 914

m/z (EI) 330 (M^+).

Compound 915

m/z (EI) 342 (M^+).

Compound 916

m/z (EI) 315 (M^+).

Compound 917

m/z (EI) 364 (M^+).

Compound 918

m/z (EI) 364 (M^+).

Compound 919

m/z (EI) 344 (M^+).

Compound 920

^1H N.M.R ($CDCl_3$) δ (ppm) 2.35 (s), 2.5 (s), 7.4 (d), 7.8 (m), 7.9 (d).

Compound 921

^1H N.M.R ($CDCl_3$) δ (ppm) 3.9 (3H, m), 6.9-7.05 (2H, m), 7.5-7.75 (2H, m), 7.95 (1H, d), 8.0 (1H, d), 8.5 (1H), 9.1 (1H).

Compound 922

m/z (EI) 328 (M^+).

Compound 946

m/z (EI) 396 (M^+).

Compound 947

m/z (EI) 368 (M^+).

Compound 948

m/z (EI) 376 (M^+).

Compound 949

^1H N.M.R ($CDCl_3$) δ (ppm) 0.1-1.5 (5H, m), 1.7-1.9 (5H, m), 2.6 (1H, t), 8.0 (1H, m), 8.55 (1H, m).

Compound 950

m/z (EI) 406 (M^+).

Compound 951

m/z (EI) 332 (M^+).

Compound 952

m/z (EI) 349 (M^+).

Compound 953

^1H N.M.R ($CDCl_3$) δ (ppm) 1.4 (3H, t), 3.0 (2H, q), 7.2 (3H, t) isomer, 7.3 (1H, d), 7.55 (1H, dd), 8.0 (1H, d, m), 8.55 (1H, d, m).

Compound 954

^1H N.M.R ($CDCl_3$) δ (ppm) 2.5 (3H, m), 7.2-7.4 (2H, m), 7.5 (1H, d), 7.9 (1H), 8.4 (1H).

Compound 955

^1H N.M.R ($CDCl_3$) δ (ppm) 2.6 (s), 4.8 (s), 7.25 (t), 7.5 (dd), 7.9 (m), 8.05 (d), 8.15 (d), 8.5 (s), 8.8 (d).

b) *O*-[3-Chloro-5-(trifluoromethyl)-2-pyridyl]hydroxylamine

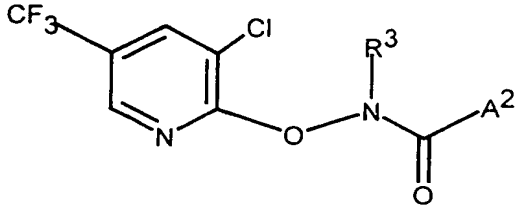
Hydrazine monohydrate (1.7 g) was added to a solution of the product from stage a) (11.3 g) in tetrahydrofuran (200 ml) and the mixture stirred for 16 hours. The mixture was then filtered and the residual solid washed with a small volume of tetrahydrofuran and ethyl acetate, then four times with a 0.02M solution of sodium hydroxide saturated with sodium chloride. The combined aqueous layers were extracted with dichloromethane (x2) and the combined organic extracts dried, filtered and evaporated to give the title compound.

Example 14

N-(3-Chloro-5-trifluoromethyl-2-pyridyloxy)-*N*-methyl-1-naphthalenecarboxamide (Compound 1017)

Iodomethane (0.82 g) was added to a stirred solution of the product from Example 13 (Compound1012) (1.93 g) and potassium *tert*-butoxide (0.61 g) in tetrahydrofuran (50 ml). The reaction mixture was stirred for 48 hours. The solvent was evaporated and the residue partitioned between ethyl acetate and saturated aqueous ammonium chloride. The aqueous layer was separated and extracted with 3 portions of ethyl acetate. The combined organic phases were dried, filtered and evaporated to give a residue which was purified by silica gel chromatography (ethyl acetate/petrol) to give the title compound, *m/z* (EI) 380 (M^+).

The following compounds of formula Ir (see Table J), i.e. compounds of general formula I where A^1 is 3-Cl-5-CF_3-2-pyridyl and L is –O-N(R^3)C(=O)-, may be prepared by methods analogous to those of Examples 13 and 14.



(Ir)

Table J

Cmp	R^3	A^2	m.p.(°C)
1001	H	5-Me-2-pyrazinyl	202-6

Example 15

2-Methyl-1,2,3,4-tetrahydro-1-naphthalenone *O*-1-[3-chloror-5-(trifluoromethyl)-2-pyridyl]oxime

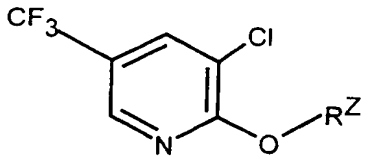
(Compound 1101)

The starting material (0.58 g) was dissolved in tetrahydrofuran (5 ml) and to this was added potassium *tert*-butoxide (0.42 g) dissolved in tetrahydrofuran (5 ml). The mixture was stirred overnight and a solution of 2,3-dichloro-5-trifluoromethyl pyridine (0.72 g) in tetrahydrofuran (2 ml) was added. The mixture was stirred for 48 hours at room temperature, then the solvent was evaporated. The residue was partitioned between ethyl acetate and water. The organic layer was isolated, dried, filtered and evaporated to yield the title product as a light yellow gum, *m/z* (EI) 354 (M^+).

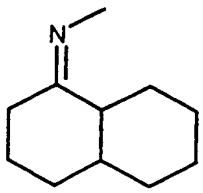
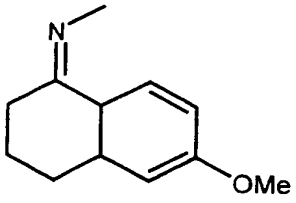
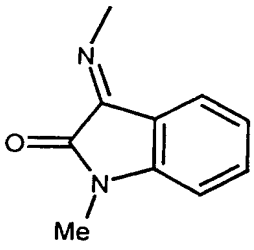
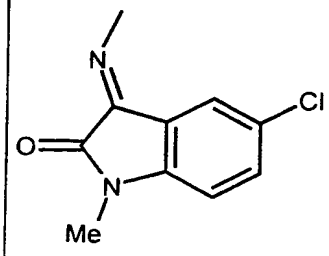
a) 2-Methyl-1,2,3,4-tetrahydro-1-naphthalenone oxime

To a solution of 2-methyl-1-tetralone (3.20 g) in methanol (5 ml) was added hydroxylamine hydrochloride (1.81 g) in methanol (15 ml) and triethylamine (2.63 g). The mixture was stirred at 65°C for 5 hours, allowed to cool and stand at room temperature for 16 hours. The solvent was evaporated and water added to the residue. The product was extracted with ethyl acetate (3 portions) and the combined extracts were dried, filtered and evaporated to give an orange oil. On standing this separated into two layers. The top layer was removed and the bottom layer slowly solidified to give the title product as an orange solid.

The following compounds of formula Iq (see Table K), i.e. compounds of general formula I where A^1 is 3-Cl-5-CF_3-2-pyridyl and L is –O-N=C(R^1)-, wherein R^1 and A^2, together with the interconnecting atoms forms a 5- or 6- membered ring, may be prepared by methods analogous to those of Example 15.



(Iq)

Cmp	R^Z	m.p.(°C)
1107		oil
1108		oil
1109		oil
1110		oil

Those compounds in Table K which do not have discrete melting points have the following characteristic mass spectral data.

Compound 1101

m/z (EI) 354 (M^+).

Compound 1102

m/z (EI) 370 (M^+).

Compound 1103

m/z (EI) 385 (M^+).

2-(3-Bromo-4-methoxyphenyl)imidazole was synthesised from 3-bromo-4-methoxybenzonitrile using a method known to the skilled chemist.

Test Example

Compounds were assessed for activity against one or more of the following:

Phytophthora infestans: late tomato blight

Plasmopara viticola: vine downy mildew

Erysiphe graminis f. sp. tritici: wheat powdery mildew

Pyricularia oryzae: rice blast

Leptosphaeria nodorum: glume blotch

Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. After a given time, plants or plant parts were inoculated with appropriate test pathogens before or after application of the compounds as appropriate, and kept under controlled environmental conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds are assessed on a score of 1 to 3 where 1 is little or no control, 2 is moderate control and 3 is good to total control. At a concentration of 500 ppm (w/v) or less, the following compounds scored 2 or more against the fungi specified.

Phytophthora infestans: 49, 102, 119, 126, 202, 214, 215, 601, 902, 912, 927, 953, 1101 and 1102.

Plasmopara viticola: 5-7, 9, 10, 12, 102, 109, 126, 214, 215, 601, 901, 907, 914, 915, 921, 926-30, 958, 1001 and 1013.

Erysiphe graminis f. sp. tritici: 501, 901, 906, 913-5, 923, 926-931, 933, 935, 936, 948-50, 952, 954, 1008, 1102, 1104, 1107 and 1108.

Pyricularia oryzae: 7, 9, 11, 17, 126, 901, 906, 907, 913, 922, 923, 926-31, 937, 938, 939 and 1001.

Leptosphaeria nodorum: 23, 51, 53, 126, 207, 208, 906, 923, 926, 929, 933, 1007 and 1109.

wherein R^b is alkyl, alkenyl, alkynyl, carbocyclyl or heterocyclyl, each of which may be substituted; or hydrogen or acyl, or two adjacent R^b groups together with the nitrogen atom to which they are attached may form a 5- or 6-membered ring.

2. A pesticidal composition comprising at least one compound as claimed in claim 1 in admixture with an agriculturally acceptable diluent or carrier.

3. A method of combating pests at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 00/08268

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 469 711 A (SUMITOMO CHEMICAL CO) 5 February 1992 (1992-02-05) examples 90-92,151	1-3
X	EP 0 288 976 A (CIBA GEIGY AG) 2 November 1988 (1988-11-02) page 8 -page 15; examples	1-3
X	EP 0 270 061 A (HOFFMANN LA ROCHE) 8 June 1988 (1988-06-08) example 16	1-3
X	DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MINN, KLEMENS: "Chalcones via a palladium-catalyzed coupling of iodoheterocycles to 1-phenyl-2-propyn-1-ol" retrieved from STN Database accession no. 115:8710 CA XP002152591 RN 134182-89-1 & SYNLETT (1991), (2), 115-16 , 1991,	1
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 04, 31 May 1995 (1995-05-31) -& JP 07 025853 A (ISHIHARA SANGYO KAISHA LTD), 27 January 1995 (1995-01-27) example 21	1-3
Y	WO 99 07687 A (AGREVO UK LTD ;COOPER IAN PAUL (GB); WEST PETER JOHN (GB); CARVER) 18 February 1999 (1999-02-18) example 19B; table B	1-3
Y	WO 98 50352 A (BRIGGS GEOFFREY GOWER ;CORNELL CLIVE LEONARD (GB); AGREVO UK LTD () 12 November 1998 (1998-11-12) page 27; example 313	1-3
Y	WO 98 42671 A (HAMPRECHT GERHARD ;BASF AG (DE); MENGES MARKUS (DE); WALTER HELMUT) 1 October 1998 (1998-10-01) the whole document	1-3
Y	WO 97 10215 A (BASF AG ;WAGNER OLIVER (DE); WETTERICH FRANK (DE); EICKEN KARL (DE) 20 March 1997 (1997-03-20) page 32 -page 33; table 4	1-3

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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